

Ion-sensitive phase transitions driven by Debye-Hückel non-ideality

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We find that the Debye-Hückel nonideality of dilute aqueous electrolytes is sufficient to drive volume phase transitions and criticality, even in the absence of a self-attracting or elastic network. Our result follows from a Landau mean-field theory for a system of confined ions in an external solution of mixed-valence counterions, where the ratio of squared monovalent to divalent ion concentration provides a temperature-like variable for the phase transition. Our analysis was motivated by long-studied volume phase transitions via ion exchange in ionic gels, but our findings agree with existing theory for volume-temperature phase transitions in charged hard-sphere models and other systems by Fisher and Levin, and McGahay and Tomozawa. Our mean-field model predicts a continuous line of gas-liquid-type critical points connecting a purely monovalent, divalent-sensitive critical point at one extreme with a divalent, monovalent-sensitive critical point at the other; an alternative representation of the Landau functional handles this second limit. It follows that critical sensitivity to ion valence is tunable to any desired valence ratio. The critical or discontinuous dependent variable can be the confinement volume; alternatively the internal electrical potential may be more convenient in applications. Our simplified conditions for ionic phase transitions to occur, together with our relatively simple theory to describe them, may facilitate exploration of tunable critical sensitivity in areas such as ion detection technology, biological switches and osmotic control.

I. INTRODUCTION

Phase transitions in charged networks, as manifested by dramatic and reversible swelling of a polymer gel, have been studied for over thirty years.^{1–3} In such gels expansion is driven by the osmotic pressure of mobile counterions that are free to exchange with an external ion population in a Donnan equilibrium.^{3,4} Osmotic pressure varies under exchange of divalent for monovalent ions, so that such systems can be critically sensitive to—among other things—the relative external concentrations of multivalent ions. Accordingly, such phase transitions have long been discussed with an eye to applications such as switches, artificial muscles⁵ and metal-ion detection,⁶ or as candidate mechanisms for essential biophysical processes.^{7,8} As in familiar liquid-vapor transitions, some element of self-attraction is always required to drive the transition; in gels, effective self-attractions are known to arise from relatively complicated network effects as theoretically described by Flory.⁹ In fact, such network behavior is by itself rich enough to yield critical behavior with no ions present.^{3,10}

Seeking a simplified framework for critical ionic sensitivity such as that observed in charged networks, we have recast the theory of ionic phase transitions into a solvable mean-field formulation, where we included in the theory a nonideality of Debye-Hückel type, which is correct in the dilute limit for all ionic solutions. We found that in principle a self-attracting network is not necessary for a discontinuous phase transition in the presence of the power-law nonideality, which itself acts as an effective self-attraction mediating an ionically driven phase transition of the gas-liquid type. Our model requires us to include a self-repulsive term to avoid runaway collapse due to the non-ideal term. In biological applications, intracellular charged proteins may play the role of confined

charges, and steric exclusion among them would naturally provide the self-repulsive term. In fact¹¹ charges on intracellular proteins in cells are present in densities such that Debye-Hückel criticality could play a role in osmotic control within organisms.

Within our mean-field theory, we find that by changing the magnitude of our self-repulsive term, we can move the system through a line of critical points. In this way, criticality is in principle tunable to occur at any desired value of external divalent ion fraction.

Our finding of Debye-Hückel criticality was made in the context of ion exchange in aqueous systems,¹² but it is in accord with established work in the context of volume-temperature transitions in charged hard-sphere fluids initiated by Fisher and Levin,^{13,14} in semiconductor electron-hole fluids, glasses, and molten salts by McGahay and Tomozawa¹⁵ and in neutral polyampholytes (overall-neutral charged polymers) by Barbosa and Levin.¹⁶

Both our simplified formulation of ionic transitions and our prediction of criticality in aqueous systems much simpler than gel networks may illuminate mechanisms of tunable critical sensitivity to ion valence or concentration that could underlie, for example, biophysical cellular functions such as homeostasis.¹¹ The theory may also lend itself to engineering applications involving ion detection. For these purposes the internal electric potential Φ , which we calculate, might be a more convenient dependent parameter than volume in applications to ion detection or in biophysical roles for critical ionic sensitivity.

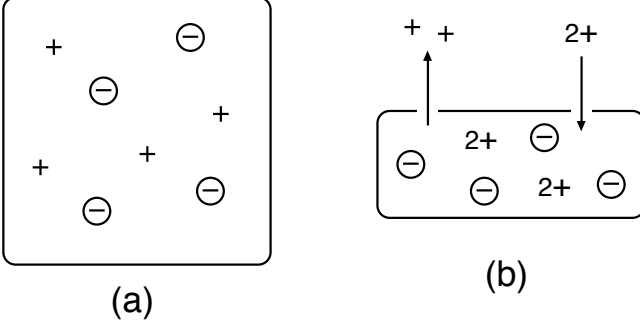


FIG. 1. Schematic mechanism for a phase transition under changing relative concentrations of mobile monovalent and divalent counterions; confined charges are chosen negative in the diagram. Divalent ions can exchange for monovalents, reducing the internal osmotic pressure while preserving approximate neutrality. An effective self-attraction of the confined-charge system can lead to a volume phase transition, with external divalent fraction serving as an effective temperature parameter.

II. DONNAN EQUILIBRIUM WITH NONIDEALITY

Consider a population of N_0 ions each of charge q_0 (of either sign, in our treatment) that may be bound to a mechanical structure, such as a polymer network, or otherwise confined within a volume permeable to counterions. These are the conditions for Donnan equilibrium^{17,18} in which osmotic pressure of excess counterions goes hand-in-hand with an internal voltage Φ , relative to outside, with the same sign as q_0 . Even for $\Phi \neq 0$, neutrality holds to a good approximation whenever the voltage drop Φ occurs only at the boundary, or more generally if $N_0 \gg C\Phi/q_0$, where C is the system capacitance.

Osmotic pressure is exerted via the electrical potential drop at the gel boundary. External concentrations of counterions may be much more dilute than the same species within the confinement volume. Nonetheless, small changes in the relative concentrations of external ions of differing valence can lead to large changes in internal counterion valence ratios and thus in the internal osmotic pressure, as sketched in Fig. 1. When effective self-attraction is present in the confined-ion system, to be supplied in our case by the non-ideality of the internal solution, phase transitions in volume and a critical point analogous to that in a gas-liquid system can occur.

The immobile ions, confined within a variable volume V , have concentration $c = N_0/V = 1/v$. Monovalent and divalent counterions with charges $q_a = -q_0$ and $q_b = -2q_0$ are introduced at external concentrations a and b , and have within V the concentrations $a' = N_a/V$ and $b' = N_b/V$. Their free diffusion in and out is controlled by the the electrical potential Φ . We introduce nonideality of mobile ions by way of a Debye-Hückel in-

teraction or correlation free energy¹⁹

$$F_{\text{DH}} = -v_B^{1/2} k_B T V \left(\sum_{\alpha} z_{\alpha}^2 c_{\alpha} \right)^{3/2} \quad (1)$$

where $q_{\alpha} = z_{\alpha}e$. The essential features of F_{DH} are that it is negative and contains mobile-ion concentrations raised to the $3/2$ power. The constant v_B is proportional to the cube of Bjerrum length. In standard aqueous conditions,

$$\frac{1}{v_B} = (12\pi)^2 \left(\frac{\epsilon k_B T}{e^2} \right)^3 \approx 3.4 \text{ molar}. \quad (2)$$

To obtain closed-form solutions, we omit confined ions from the sum, and replace the factor $(a' + 4b')^{3/2}$ by $(a' + 2b')^{3/2}$, which will equal $c^{3/2}$ once neutrality is imposed. Thus we employ the Debye-Hückel-like interaction term

$$F_{\text{int}} = -v_B^{1/2} k_B T V (a' + 2b')^{3/2}. \quad (3)$$

With $a' = N_a/V$ and $b' = N_b/V$ and taking derivatives,

$$P_{\text{int}} = -\frac{\partial F_{\text{int}}}{\partial V} = -\frac{1}{2} v_B^{1/2} k_B T (a' + 2b')^{3/2} \quad (4)$$

$$\frac{\partial F_{\text{int}}}{\partial N_a} = k_B T \ln \gamma_a = -\frac{3}{2} k_B T v_B^{1/2} (a' + 2b')^{1/2} \quad (5)$$

$$\frac{\partial F_{\text{int}}}{\partial N_b} = k_B T \ln \gamma_b = -3 v_B^{1/2} k_B T (a' + 2b')^{1/2} \quad (6)$$

where activity coefficients γ_a and γ_b for the monovalent and divalent ions are defined by^{20,21}

$$\mu_a = \mu_a^0 + k_B T \ln(\gamma_a a). \quad (7)$$

Proportionality of $\ln \gamma$ to the square root of ionic concentration is the hallmark of Debye-Hückel behavior, a theory appropriate to low ionic strength.^{22,23} The free energy, with Φ externally controlled, is

$$F(N_a, N_b, V, \Phi) = F_0(V) + F_{\text{int}}(N_a, N_b, V) + (N_0 - N_a - 2N_b)q_0\Phi + N_a k_B T \left[\ln \frac{N_a}{c_0 V} - 1 \right] + N_b k_B T \left[\ln \frac{N_b}{c_0 V} - 1 \right]. \quad (8)$$

Here $F_0(V)$ describes mechanical constraints on the immobile ions, such as a polymer network carrying the fixed ions or a membrane containing them. The logarithmic terms are the ideal free energy of the mobile ions, and c_0 is a concentration scale which will cancel out. The mechanical contribution to pressure is $-\partial F_0/\partial V = P_0$ (equivalently a function of v or c). The overall pressure and the chemical potentials $\mu_a = \partial F/\partial N_a$ and $\mu_b = \partial F/\partial N_b$ are

$$P = P_0(v) + (a' + b')k_B T + P_{\text{int}} \quad (9)$$

$$\mu_a = -q_0\Phi + k_B T \ln \left(\frac{\gamma_a a'}{c_0} \right) \quad (10)$$

$$\mu_b = -2q_0\Phi + k_B T \ln \left(\frac{\gamma_b b'}{c_0} \right) \quad (11)$$

If we set $\mu_a = k_B T \ln(a/c_0)$ and $\mu_b = k_B T \ln(b/c_0)$, a and b become effective concentrations, referred to an ideal external solution. To fix Φ , we impose neutrality, $c = a' + 2b'$, and introduce a dimensionless potential

$$\phi = q_0 \Phi / k_B T \quad (12)$$

which will always be positive, since Φ will always be of the same sign as q_0 . We have altogether

$$P = P_0(N_0/c) + \frac{1}{2}(a' + c)k_B T - \frac{1}{2}v_B^{1/2} c^{3/2} k_B T \quad (13)$$

$$\phi = \ln(a'/a) - \frac{3}{2}v_B^{1/2} c^{1/2} \quad (14)$$

$$2\phi = \ln(b'/b) - 3v_B^{1/2} c^{1/2} \quad (15)$$

which, together with $c = a' + 2b' = N_0/v$, we will solve to find $P(v)$. Combining the equations involving ϕ , putting $2b' + a' - c = 0$ for neutrality, and solving yields

$$a' = \left(\frac{a^2}{4b}\right) \left[\left(1 + (8b/a^2)c\right)^{1/2} - 1 \right] \quad (16)$$

We define the dimensionless divalent parameter

$$\beta = \frac{8b}{v_B a^2}. \quad (17)$$

To motivate the ratio $\beta \sim b/a^2$ by a chemical analogy, imagine $N_0/2$ divalent counterions B^{2+} , complexed with an N_0 -valent entity C^{N_0+} , cooperatively exchanging with N_0 monovalent counterions A^+ according to



Equilibrium, in the sense of mass action, then gives

$$\frac{[CB_{N_0/2}]}{[CA_{N_0}]} = K \frac{[B^{2+}]^{N_0/2}}{[A^+]^{N_0}} = \text{const} \times \left(\frac{b}{a^2}\right)^{N_0/2}. \quad (19)$$

As $N_0 \rightarrow \infty$, the monovalent-divalent exchange $CB_n \leftrightarrow CA_{2n}$ becomes discrete at a particular value of b/a^2 .

III. PHASE BOUNDARY

The dimensionless pressure $p(v) = Pv_B/k_B T$ is

$$p(v) = p_0(v) + \frac{1}{2} \frac{v_B}{v} + \frac{1}{\beta} \left[\left(1 + \beta \frac{v_B}{v}\right)^{1/2} - 1 \right] - \frac{1}{2} \left(\frac{v_B}{v}\right)^{3/2} \quad (20)$$

where $p_0 = P_0 v_B / k_B T$. To make the system stable against collapse to $v = 0$ (due to the interaction term) we require that $p_0(v)$ include a repulsion diverging faster than $1/v^{3/2}$. We will use the minimal choice

$$p_0(v) = \alpha \left(\frac{v_B}{v}\right)^2 > 0 \quad (21)$$

with α dimensionless. The dimensionless electrical potential is

$$\phi = \ln \frac{2}{\beta} \left[\left(1 + \beta \frac{v_B}{v}\right)^{1/2} - 1 \right] - \frac{3}{2} \left(\frac{v_B}{v}\right)^{1/2} - \ln(v_B a). \quad (22)$$

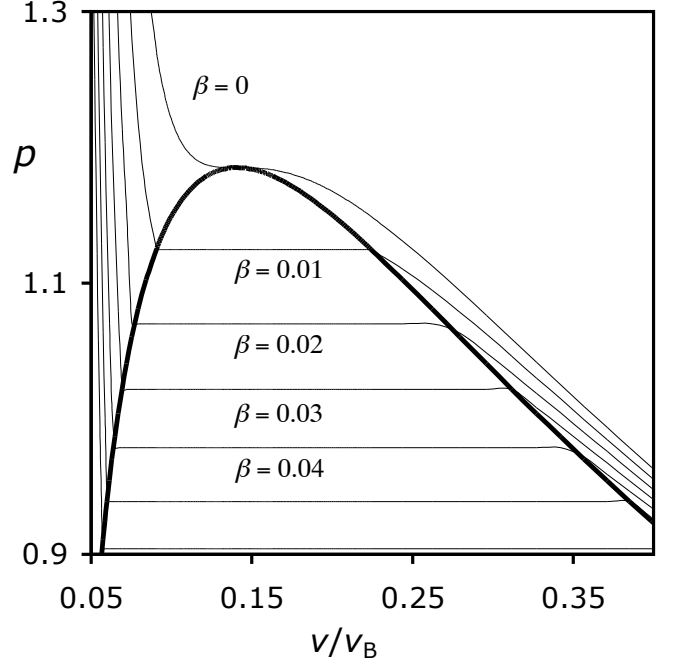


FIG. 2. Coexistence diagram in dimensionless volume and pressure for a system tuned by repulsion α to the monovalent ($\lambda = 1$) critical point. The divalent parameter β rises from zero upon addition of divalent ions, so that $\beta < 0$ is not possible for $\lambda = 1$. In similar coexistence diagrams for $0 < \lambda < 1$, the upper region will be accessible.

From the Gibbs-Duhem relation (at constant T , or here β) we obtain the chemical potential, linking coexisting v and v' at specified β , as

$$\begin{aligned} \mu(v) &= pv - \int p(v) dv \\ &= \frac{2\alpha}{v} - \frac{3}{2v^{1/2}} - \ln \left[v + \sqrt{v(v+\beta)} \right] + \frac{1}{2}. \end{aligned} \quad (23)$$

Self-intersections of the curve $(p(v), \mu(v))$ yield phase boundaries as in Figs. 2 and 3.

IV. CRITICAL LINE

We solve our model in terms of the parameter

$$x = \sqrt{\frac{v_B}{v}}. \quad (24)$$

At a critical point the conditions $p'(v) = p''(v) = 0$ and $p'(x) = p''(x) = 0$ are equivalent. Regarding the critical value of p as a function of x and β , and introducing the parameter $\lambda = 1/\sqrt{1+\beta_c x_c^2}$, we have the x -derivatives

$$\tilde{p}_x = x_c \left[4\alpha x_c^2 - \frac{3}{2}x_c + 1 + \lambda \right] = 0 \quad (25)$$

$$\tilde{p}_{xx} = 12\alpha x_c^2 - 3x_c + 1 + \lambda^3 = 0 \quad (26)$$

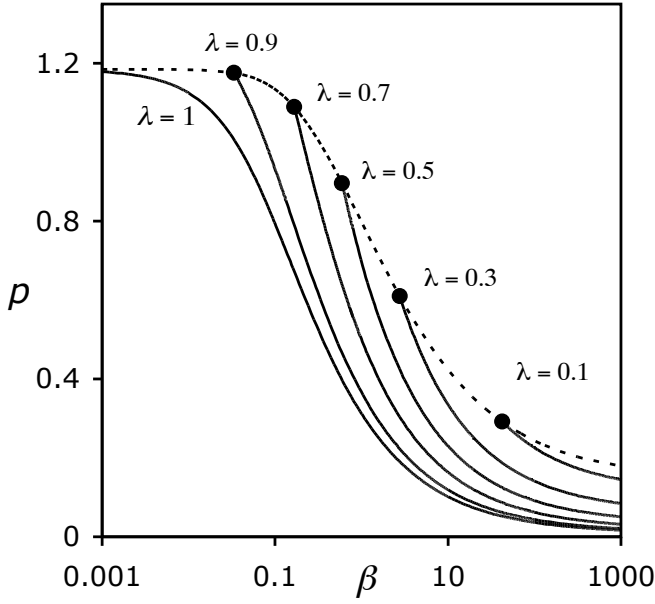


FIG. 3. Critical line (dotted) connecting the monovalent ($\lambda = 1$) and divalent ($\lambda = 0$) critical points. The divalent parameter is β and p is dimensionless pressure. Selected critical points and their phase boundaries (solid) are shown. The phase boundary becomes inaccessible (moving to $\beta > \infty$) for the critical point at $\lambda = 0$.

Eliminating α in favor of λ gives the line of critical points

$$p_c = x_c^2 \left[\frac{1}{12} (1 - 6\lambda + \lambda^3) + \lambda / (1 + \lambda) \right] \quad (27)$$

$$x_c = \frac{2}{3} [2 + 3\lambda - \lambda^3] \quad (28)$$

$$\alpha_c = (1 + 2\lambda - \lambda^3) / 4x_c^2 \quad (29)$$

$$\beta_c = 1 / (x_c^2 \lambda^2) \quad (30)$$

The interval $0 \leq \lambda \leq 1$ corresponds to $\infty \geq \beta \geq 0$. Although we view $\alpha(\lambda)$ as the mechanism by which ionic critical points can be tuned, we can also view $\alpha_c = \alpha(\lambda)$ as a critical value of the repulsion strength. With ionic conditions fixed, we could drive transitions by modulating α , analogous to transitions in ionic gels induced by variation of solvent composition.¹

About each critical point, with $\delta v = v - v_c$ and $\delta\beta = \beta - \beta_c$, we construct a Landau expansion for the pressure,

$$p(\beta, \epsilon) = p_c - A\delta\beta + B\delta\beta\epsilon - C\epsilon^3 \quad (31)$$

where $\epsilon = \delta v + \kappa\delta\beta$ is an order parameter linear in δv and $\delta\beta$. In a potential application, we imagine tuning a system to a critical point, $\beta = \beta_c$ and $p = p_c$. Within mean-field theory, when the divalent ratio is changed by $\delta\beta = \beta - \beta_c$ one predicts a singular expansion or contraction

$$\epsilon \approx -(A/C)^{1/3} (\delta\beta)^{1/3} \quad (32)$$

where the cube root is taken with the same sign as $\delta\beta$. As discussed below, this singular behavior in volume might

in practice be better monitored via the electric potential than the volume change δv or ϵ .

To evaluate the Landau coefficients, we expand the pressure around the critical point, to third order in $\delta v = v - v_c$ and to first order in $\delta\beta$, giving

$$p(v, \beta) \approx p_c + \tilde{p}_\beta \delta\beta + \tilde{p}_{v\beta} \delta\beta\epsilon + \frac{1}{6} \tilde{p}_{vvv} \epsilon^3 \quad (33)$$

where β and v subscripts denote partial derivatives and \tilde{p} , \tilde{p}_v , etc. are critical values. We have chosen $\kappa = \tilde{p}_{vv\beta} / \tilde{p}_{vvv}$ to eliminate an ϵ^2 term. Evaluating the various derivatives, the Landau parameters along the critical line are

$$A = \frac{1}{2} x_c^4 \lambda^3 / (1 + \lambda)^2, \quad B = \frac{1}{4} x_c^6 \lambda^3 \quad (34)$$

$$C = \frac{1}{48} x_c^8 [2 + 12\lambda - 7\lambda^3 + 3\lambda^5] \quad (35)$$

$$\kappa = (\lambda^3 / x_c) (\lambda^2 + 1) / (8x_c \alpha_c - \beta_c \lambda^5) \quad (36)$$

where x_c and α_c are known functions of λ from Eqs. (28) and (29). C has no zeros within $0 \leq \lambda \leq 1$, while κ is zero only at $\lambda = 0$. At the monovalent critical point ($\beta = 0$, i.e. $\lambda = 1$) Eqs. (27) through (30) yield $p_c = 32/27 \approx 1.185$, $x_c = 8/3 \approx 2.67$, $\alpha_c = 9/128 \approx 0.0703$, the Landau coefficients are

$$A = 2^9 / 3^4 \approx 6.321 \quad (37)$$

$$B = 2^{16} / 3^6 \approx 89.90 \quad (38)$$

$$C = 5(2^{21} / 3^8) \approx 1598.2 \quad (39)$$

and the order parameter is $\epsilon = \delta v + (1/2)\delta\beta$. Here the system enters coexistence for any value of $\beta > 0$, with $\epsilon \approx -(0.158)\beta^{1/3}$. A system tuned to the monovalent critical point moves with infinite response towards a smaller volume with the introduction of any divalents. In the liquid-gas analogy, this path follows the critical isobar.

At the purely divalent critical point ($\beta = \infty$, $\lambda = 0$) both A and B vanish, but we can here characterize the line of critical points by the alternative parameterization

$$p(\beta, \epsilon) = p_c + A'\delta(\beta^{-1/2}) - B'\delta(\beta^{-1/2}) - C\epsilon^3 \quad (40)$$

$$A' = x_c(1 - \lambda)^{3/2} / (1 + \lambda)^2 \quad (41)$$

$$B' = \frac{1}{2} x_c^3 (1 - \lambda^2)^{3/2} \quad (42)$$

The parameter $\beta^{-1/2}$ is proportional to the monovalent concentration at fixed divalent concentration. The volume singularity (32) can be rewritten as

$$\epsilon \approx + \left[\frac{A'}{C} \delta(\beta^{-1/2}) \right]^{1/3} \quad (43)$$

where again the cube root has the same sign as its argument. At the divalent critical point ($\beta = \infty$, $\lambda = 0$) Eqs. (27) through (30) yield $p_c = 4/27 \approx 0.1481$, $x_c = 4/3$, $\alpha_c = 9/64 \approx 0.1406$,

$$A' = 4/3, \quad B' = 32/27 \approx 1.185 \quad (44)$$

$$C = 2^{13} / 3^9 \approx 0.4162 \quad (45)$$

For this divalent critical point at $\beta_c^{-1/2} = 0$, the order parameter is simply the volume, $\epsilon = \delta v$. A purely divalent system that is tuned to be critical moves with infinite response towards a larger volume with the introduction of any monovalents, as $\delta v \approx (1.214) \beta^{-1/6}$.

Returning to the dimensionless potential $\phi = q_0 \Phi / k_B T$ in Eq. (22), along the critical line with a constant we find

$$\left[\frac{\partial \phi}{\partial v} \right]_c = \frac{3 x_c^3}{4 v_B} \left[\frac{1 + 2\lambda - \lambda^3}{2 + 3\lambda - \lambda^3} \right] \quad (46)$$

Eq. (46) is nonzero along the entire line of critical points. Since $\delta \phi \approx (\partial \phi / \partial v)_c \delta v$, the potential will always exhibit the same power-law singularity as the volume. In engineering applications, the internal electric potential may well be a more convenient dependent parameter than volume. In a cell-biological context, membrane electrical potential would be a likely route by which critical ion sensing could be reported.

V. CONCLUSIONS

Our simplified conditions for criticality to occur in aqueous solutions, and our mean-field framework for analyzing them, are intended to motivate investigation of ionic phase transitions in ever simpler systems. As a fascinating analogue of liquid-gas transitions, and in the context of ionic gels, such transitions have been a topic of discussion for many years. Potential applications such as metal-ion detection and electrical sensitivity^{5,6} should remain applicable to phase transitions as discussed here. Of particular interest is our finding of a line of critical points, such that ion-sensitive criticality is in principle tunable to occur at any value of the divalent fraction.

We arrived at our finding of Debye-Hückel criticality¹² in the context of swelling transitions in ionic gels, a line of experimental and theoretical work initiated by T. Tanaka, but subsequently found this conclusion to be in accord with a distinct line of theory originating with Fisher and Levin¹³ for temperature-density phase transitions in charged hard-sphere fluids, and of McGahay and Tomozawa¹⁵ for transitions in electron-hole fluids in semiconductors, glasses, and molten salts. Subsequent theory by Barbosa and Levin¹⁶ focused on neutral polyampholytes. Our treatment of nonideal Donnan equilibrium remains somewhat more phenomenological than that of these workers, who employed ion-pairing refinements of Bjerrum²⁴ and Fuoss²⁵ to obtain quantitatively accurate phase boundaries within their explicitly defined models.¹³ For simplicity, we have remained

within a dilute screening limit, even within the confined-ion region.

With regard to biological systems, we are applying the results here to biological mechanisms¹¹ such as homeostasis (control of ion concentration) and cell volume control, and in fact find that ionic levels in cells and charges on intracellular proteins do fall within ranges appropriate for Debye-Hückel criticality to play a role.

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